IMPACT OF NANOCLAY ON THERMAL, AND STATIC AND DYNAMIC MECHANICAL PROPERTIES OF BAMBOO FIBER REINFORCED UNSATURATED POLYESTER COMPOSITES

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In this article, the effects of nanoclay (NCL) filler on thermal and static and dynamic mechanical properties of bamboo fiber reinforced unsaturated polyester (BP) composites were explored. BP composites were prepared with 20 wt% reinforcement of bamboo fiber, and hybrid NCL filled bamboo fiber reinforced unsaturated polyester (NCBP) were prepared by incorporation of NCL in amounts ranging from 1 to 7 wt% (named as 1NCBP, 3NCBP, 5NCBP and 7NCBP, with reference sample – 0NCBP (BP)), using the hand layup process, followed by curing in a compression moulding machine at constant pressure (20 bar). The fabricated BP and NCBP hybrid composites were tested for static mechanical properties as per ASTM standards. By using a dynamic analyser, viscoelastic properties of the composites, such as storage modulus (E'), loss modulus (E") and damping factor (Tanδ), were investigated. Results revealed that both static and dynamic mechanical properties of the BP composites increased with an increase in NCL loading. Amongst the nanocomposites, 5NCBP was found superior, however, beyond the optimal amount of 5 wt% NCL, the properties of the materials suffered because of nanoclay agglomeration and poor interfacial bonding between fiber, matrix and filler. The glass transition temperature (T_g) of the BP composite increased from 109.88 °C to 117.73 °C after adding NCL. Thermogravimetric analysis (TGA) results showed that the presence of NCL delayed thermal degradation of the NCBP nanocomposites and thus improved thermal stability. Mechanically fractured samples of NCBP composites were exposed further by field emission scanning microscopy (FESEM) analysis to understand the failure mechanism they endured.

Keywords: bamboo fiber, unsaturated polyester, nanoclay, static and dynamic mechanical, FESEM

INTRODUCTION

In recent decades, due to the advancement of technologies, researchers have revealed promising outcomes of utilizing natural fibers as a reinforcement agent in polymer composites.[1,2] The automotive, packaging, and construction sectors have already implemented the manufacturing of some components from natural fiber polymer composites (NFPCs).[3] It is expected that the worldwide market of NFPCs will rise by compounded growth of 10.6% in the period 2019-2025.[4] The main intention is not only to valorize natural fibers, but also to curb the adverse impact of using synthetic composites on the environment.[4,5] Moreover, natural fibers, such a bamboo, flax, kenaf, hemp, and jute, are low density, ecofriendly, biodegradable and relatively high strength.[6-8] Thus, natural fibers can be a better choice in preparing polymer composites than their archrivals – synthetic fibers (glass, carbon, and Kevlar fibers).[9-13]

Hybrid polymer composites (HPCs) are prepared by reinforcing a matrix with two or more types of fibers/fillers.[14] An interesting feature of HPCs is that the reinforcement agents used can compensate for each other's limitations.[15] Thus, most research findings showed that HPCs exhibited better mechanical, thermal, and moisture absorption properties than mono-fiber reinforced polymer composites.[16] Though NFPCs, either hybridized or single fiber, have the upper hand in specific features over synthetic fibers, their usage is still limited because of their high moisture absorption, low thermal strength, and poor compatibility with the polymer matrix, regardless of the type of fiber used: flax, bamboo, jute, hemp *etc*.[13] However, such characteristics of the composites can be improved by inclusion of nanomaterials. Advanced technology breakthrough in nanoscience paved the way for developing novel polymer nanocomposites. Commonly used nanofillers are nanoclay, carbon nanotubes, graphene, carbon nanofibers, and other organic and inorganic fillers.[17] These nanofillers modify the polymer matrix to enhance intrinsic properties. Amongst the nanofillers, nanoclay is widely acclaimed and used, due to its affordability and beneficial properties for diverse applications. Researchers have reported that the inclusion of nanoclay in NFPCs enhanced the dynamic mechanical properties of the composites, as nanoclay alters the relaxation behavior of the polymer chain by intensely engaging with both fiber and matrix.

In recent years, several studies have shown that the impregnation of nanoclay in natural fiber hybrid composites has a promising impact on both static and dynamic mechanical properties of the composites. Nanoclay in kenaf mat/bamboo mat fiber reinforced epoxy composites enhanced their mechanical and dynamic mechanical properties.[4] Rajesh *et al.*[18] examined the dynamic mechanical properties of the nanoclay filler jute/banana polyester composites. Results showed that the storage modulus and glass transition temperature of the intra-ply polyester hybrid composites increased with an increase in the nanoclay content. Kushwaha *et al.*[19] found a 16.25% improvement in the elastic modulus of the epoxy/bamboo mat/MMT clay hybrid composites at 1% clay loading. Moreover, clay also played a vital role in increasing tensile and flexural properties of the hybrid composites. Kenaf/epoxy hybrid composites were also prepared by reinforcement with organically modified MMT nanoclay. The kenaf/epoxy hybrid nanocomposites exhibited better tensile, elongation break and toughness properties, as reported by Saba *et al.*[20] Enhanced mechanical, thermal and vibrational properties were exhibited by nanoclay filler glass fiber reinforced vinyl ester composites, as reported by Chandradass *et al.*[21] Seetharaman Arulmurugan *et al.*[22] found that the inclusion of 5 wt% of nanoclay in jute fiber reinforced unsaturated polyester composites has improved their mechanical and viscoelastic properties. Particularly hybrid nanocomposites having 25 wt% of jute fiber and 5 wt% nanoclay showed a 5.5% increase in glass transition temperature. In another study, an enhancement in the modulus of elasticity and rupture of nanoclay filled bamboo/polyvinyl alcohol hybrid composites was reported.[23]

From the literature survey, it can be summarized that impregnation of nanoclay in natural fiber composites is a method that has gained attention due to the enhanced mechanical, viscoelastic and thermal performance of the resulting materials. However, to date, there is limited work reported on nanoclay addition to unsaturated polyester-based composites. Thus, the present study utilizes bamboo fiber and nanoclay to reinforce an unsaturated polyester matrix to prepare hybrid composites. The main objective of the study was to study the effect of nanoclay inclusion on the static and dynamic mechanical and thermal properties of the hybrid nanocomposites, compared with those of neat composites. It is expected that the incorporation of nanoclay material in the bamboo/polyester composites would improve the aforementioned properties, without affecting the mass of the composites. Eventually, the study would reveal if these developed nanoclay filled bamboo fiber reinforced unsaturated polyester composites could be utilized for load bearing structure applications, particularly in the automotive, building and construction sectors.

EXPERIMENTAL

Materials

The matrix material used was unsaturated polyester (USP) resin supplied by the M/S Vasavibala Resins Private Limited, Chennai, India. In order to enhance the curing process of USP, methyl ethyl ketone peroxides (MEKP) and cobalt naphthenate were used as catalyst and accelerator, respectively, purchased from the same supplier. From the local Coimbatore vendors, unidirectional bamboo fibers were procured for preparing the hybrid composites. Nanoclay (NCL) (Nanocloisite, with 98% purity) was used as a secondary reinforcement agent, and was purchased from Sigma Aldrich, Bengaluru, India. The FESEM image and energy dispersive X-ray (EDX) spectrum of the NCL filler are shown in Figure 1. The properties of the bamboo fibers, USP and NCL filler are presented in Table 1.

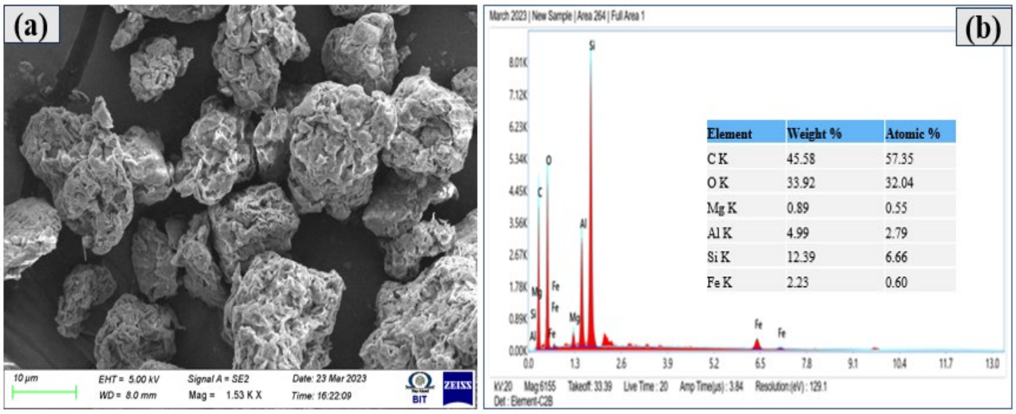

Figure 1: (a) FESEM image and EDX result of nanoclay

Table 1
Properties of the raw materials used

Raw material	Grade	Characteristics
Bamboo fiber (unidirectional)	-	Cellulose: 69-73% Hemicelluloses: 11-12.49% Lignin: 9.5-10.2% Density: 0.85-0.91 g/cc
Nanoclay	Cloisite 93A	Bulk density: 0.1659 g/cc Average size: 10-15 µm Color: light grey; non-soluble in water
Unsaturated polyester (USP) resin	VB4503	Density: 1.2 g/cc Viscosity: 500-600 cps Gel time: 15-20 mins

Fabrication of BP and NCBP hybrid composites

In the first phase of the preparation, USP resin was thoroughly mixed with the catalyst MEKP at 1.5%, according to the directions of the suppliers. A known weight fraction of the NCL filler was mixed with the mixture of USP resin and MEKP and subjected to magnetic stirring to ensure uniform distribution of the NCL particles. Afterwards, the mixture of USP resin containing NCL was added with the 1.5% cobalt naphthenate to induce the curing process. In the subsequent second phase of the preparation, the required weight fraction of the unidirectional bamboo fibers were laid on the bottom of a metal mould (235 mm × 235 mm × 3.5 mm), upon which the mixture prepared in the first phase containing USP resin and NCL filler was poured. By means of a metallic roller and a thin metal sheet, the resin mixture was uniformly spread over the bamboo fibers. This step was repeated until four layers of the bamboo fibers were stacked and closed with the support of the top metal mould. In the third phase of the processing, the mould system was subjected to the high-pressure compression in the compression moulding machine. The system was allowed to cure at room temperature and pressure (10 bar). After 24 hours of the curing process, NCL filled bamboo fiber reinforced unsaturated polyester (NCBP) hybrid composites were taken off the mould, and cut as per ASTM standards for testing their properties.

Figure 2 illustrates the fabrication of the NCBP hybrid composites. The formulations of the NCBP hybrid composites prepared in this work, with their denotation, are shown in Table 2.

Mechanical tests

BP and NCBP test specimens were tested in accordance with ASTM standards, as indicated in Figure 3: the tensile test – as per ASTM D638, flexural test – as per ASTM D790, impact test and shore D hardness test – as per ASTM D256 and ASTM D2240, respectively. Tensile and flexural tests were performed under constant crosshead speed of 5 mm/min. Surface morphology of the NCL filler and mode of failures endured by the NCBP specimens were examined using a field emission electron microscope (Carl Zeiss Sigma-300, Schottky FEG).

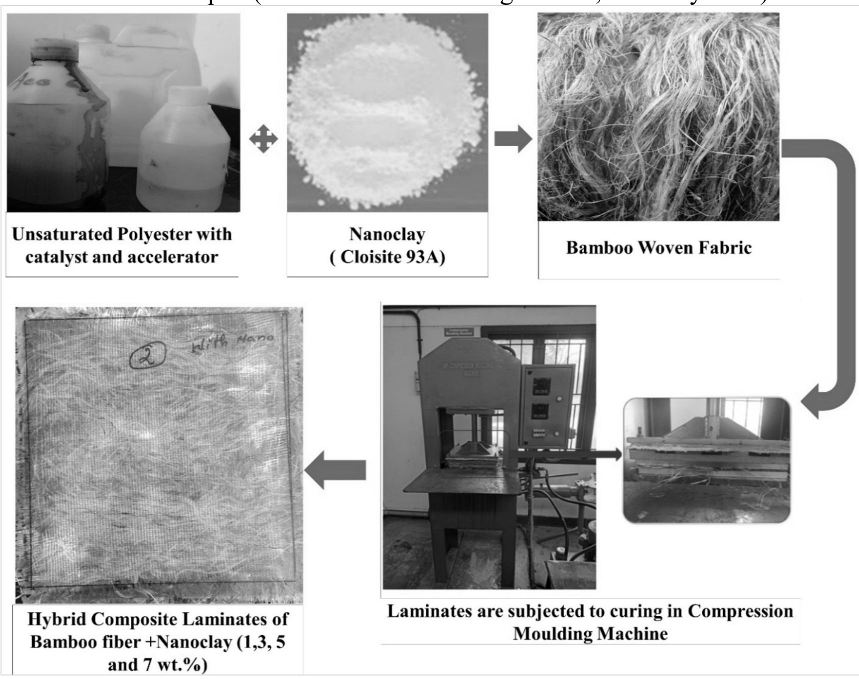

Figure 2: Fabrication of NCBP hybrid composites

Table 2
Composition of NCBP hybrid composites

Denotation	Stacking sequence	Weight (gm)				Thickness (mm)	Density (g/cc)
		W_{BF}	W_{NCL}	W_m	W_{TC}		
0NCBP (BP)	BF(0°)+BF (90°)+BF(0°)+BF (90°)	50	0	225	275.00	3.5±0.25	1.1223
1NCBP	BF(0°)+BF (90°)+ BF(0°)+BF (90°)	50	2.25	225	277.25	3.5±0.25	1.1324
3NCBP	BF(0°)+BF (90°)+ BF(0°)+BF (90°)	50	6.75	225	281.75	3.5±0.25	1.1366
5NCBP	BF(0°)+BF (90°)+ BF(0°)+BF (90°)	50	11.25	225	286.50	3.5±0.25	1.1467
7NCBP	BF(0°)+BF (90°)+ BF(0°)+BF (90°)	50	15.75	225	290.75	3.5±0.25	1.1389

BF – bamboo fiber; (0°) and (90°) – orientation of the BF; NCL – nanoclay filler; W_{BF} – weight of bamboo fibers; W_m - weight of matrix; W_{NCL} – weight of nanoclay; W_{TC} - total weight of the composite

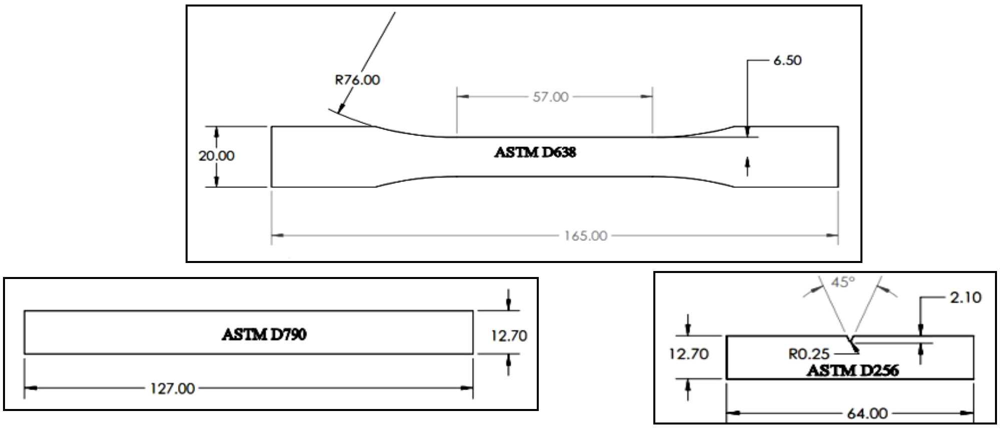

Figure 3: BP and NCBP hybrid composites prepared as per ASTM standards for: (a) tensile test (b) flexural test (c) impact test (all dimensions are in mm)

Dynamic mechanical analysis (DMA)

NCBP hybrid composite specimens were tested for viscoelastic properties in a dynamic mechanical analyser (DMS 6100, SII Nanotechnology, Japan) in the three-point configuration mode. The test was performed for the temperature range from 30 °C to 180 °C, at a heating rate of 5 °C min^{-1}, at a constant frequency of 10 Hz. Dynamic mechanical properties of the materials, namely, storage modulus (E'), loss modulus (E"), glass transition temperature (T_g), and damping factor (Tanδ), were studied.

Thermal gravimetric analysis (TGA)

The thermal degradation behavior of the NCBP hybrid composites was analyzed by recording TG thermograms for 5–9 mg samples using a Netzsch STA 2500 (Regulus, Germany). The thermal stability of the specimens was recorded in Proteus software for temperatures ranging from room temperature to 650 °C, with a heating rate of 10 °C/min under pure air (N_2/O_2: 80/20). The gas flow rate for the testing was 60 mL/min for protective (Nitrogen) and 40 mL/min for purge (air).

Vicat softening temperature (VST)

VST tests were conducted for the NCBP hybrid composites in accordance with ASTM D 1525. NCBP specimens were placed on the supporting platform, with a needle placed 1 mm away from the surface of the specimen. VST is the temperature at which the needle penetrates 1 mm distance.

RESULTS AND DISCUSSION

Mechanical behavior of BP and NCBP hybrid composites

Tensile strength

The tensile strength test results of the BP and NCBP hybrid composites are shown in Figure 4. From the plot, it can be seen that tensile strength increases with an increase in the NCL in BP composites. However, beyond 5 wt% NCL, the tensile property drops. Amongst the fabricated composites, the 5NCBP hybrid composites displayed the highest tensile strength – of 49.77 MPa, whereas the neat BP composites showed 20.02 MPa, indicating an enhancement by nearly 148.60%. This may be explained by the fact that the dispersed NCL in the matrix phase hindered crack propagation and failure. Moreover, the uniformly distributed NCL filler improved interfacial bonding strength, contributing to enhanced tensile property, as strong bonding facilitates smooth stress transfer from the matrix to the reinforcement agent.

Comparing between 1NCBP and 3NCBP, no substantial changes in tensile strength are observed. However, between 5NCBP and 7NCBP, an 18.94% difference in tensile strength is noted, which shows that the addition of NCL beyond 5 wt% is not favorable for the hybrid composites. Moreover, though the tensile strength of 5NCBP is higher than that of 1NCBP and 3NCBP, the decrement of the strength for over 5 wt% filler inclusion may be attributed to the weakening of the fiber-matrix interphase, resulting from the agglomeration of the NCL particles. On the other hand, an increase in the tensile strength can be related to the density of the material. From Table 2, it can be seen that the density of the composite increased with the increase in the NCL content. However, beyond the optimal loading of 5 wt%, density decreases. The improvement in the tensile strength may be attributed to the formation of hydrogen bonds between the cellulosic fibers during the hot-pressing process.[39] By hydrogen bonding, the interfacial strength between the filler, fiber and matrix might have increased, resulting in uniform stress transfer between the reinforcement agent and the matrix.

Flexural strength

The effect of NCL on the flexural strength of the BP and NCBP hybrid composites is illustrated in Figure 5. The flexural strength of the NCBP hybrid composites increases with the increase in the loading of NCL particles. A similar trend to that of the tensile property is noted for the flexural behavior of the NCBP hybrid composites. It is evident from Figure 3 that the flexural strength of the NCBP hybrid composite outperformed that of neat BP composites. Superior bending strength of 49.65 MPa is exhibited by 5NCBP composites, followed by 7NCBP, 3NCBP, and 1NCBP composites. However, it is interesting that there is no significant difference in the flexural strength between 7NCBP and 3NCBP composites. The flexural strength of the composites highly relies on the reinforcement used. This study utilized bamboo fiber, which is a quite stiff material, thus affecting the bending property of the composites. Thus, a stiffer reinforcement material results in good bending strength. From the plot in Figure 5, it can be noted that, compared to neat BP composites, there is a 20.22%, 25.12%, 35.92%, and 28.09% improvement in the bending strength of 1NCBP, 3NCBP, 5NCBP, and 7NCBP, respectively, which indicates the strong impact of the NCL in the BP composites. NCL addition has the potential to improve the fracture resistance of the NCBP hybrid composites. Under the bending load applied, the responsibility of the matrix and fillers is to transfer this load to the rigid member (fibers) via shear forces at the junctions, which demands strong bonding among the matrix, filler, and fibers in the NCBP hybrid composites. In this context, an enhancement in the flexural strength of the NCBP hybrid composites may be due to the strong adherence between the fiber, filler and matrix. The inclusion of NCL in BP hybrid composites has improved the toughness of the materials, ensuring stronger interfacial interaction between NCL filler–fibers and USP matrix.

Impact strength property

Figure 6 depicts the impact energy endured by BP and NCBP hybrid composites. It is evident from the plot that the impact strength of the NCBP hybrid composites increases with the increase in the loading of NCL up to 5 wt%, and beyond that, it drops. Compared to the neat BP composites, a significant improvement of 20.36%, 35.25%, 60.88%, and 41.57% in the impact strength of 1NCBP, 3NCBP, 5NCBP, and 7NCBP, respectively, was recorded, which indicates the positive impact of NCL in the BP composites. Amongst the prepared NCBP composites, 5NCBP showed the highest improvement, being nearly 1.75 and 2.95 times higher than 1NCBP and 3NCBP hybrid composites, respectively. This improvement may be attributed to the strong interfacial adhesion of fiber-filler-matrix, which could have aided in smooth distribution of the load from the USP matrix to the primary reinforcement member – bamboo fiber.

A comparison of mechanical properties of the NCBP composites with those of other bamboo fiber-based composites is presented in Table 3. When compared with other bamboo/polymer composites, NCBP composites in the present work exhibited better mechanical properties. However, the absence of glass fiber reinforcement in the NCBP composite is very evident compared to our previous report,[38] considering the nearly 66.66% and 63.36% lower tensile strength and flexural strength of the composites, respectively.

Shore D hardness

Figure 7 depicts the shore D hardness value of the BP and NCBP hybrid composites. The shore D hardness value increases with the increase in wt% of NCL particles and the highest value is exhibited by the 5NCBP hybrid composites, containing 5 wt% of NCL filler as a secondary reinforcement agent. The inclusion of NCL in the BP composites could have enhanced the resistance to the plastic deformation since hardness behavior of the composites relies on the plastic deformation of the material system. Therefore, the shore D hardness value of the NCBP hybrid composites improved with the increasing loading of NCL. Apart from that, it is also important to point out that uniform distribution of the NCL could have reduced the voids in the NCBP hybrid composites, which would have also paved the way for incremental rise in the hardness of the composites.

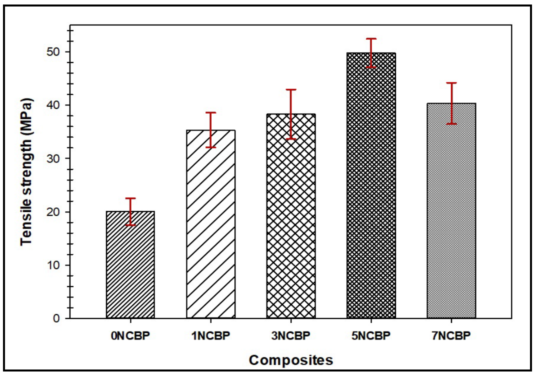

Figure 4: Tensile strength of BP and NCBP hybrid composites

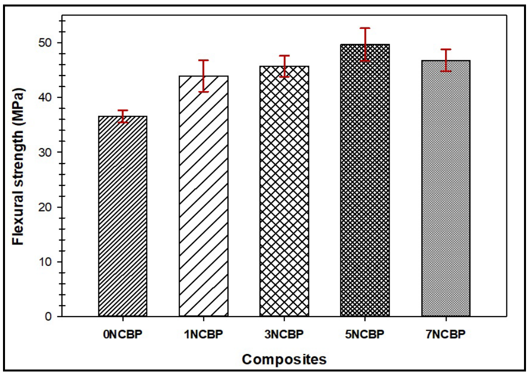

Figure 5: Flexural strength of BP and NCBP hybrid composites

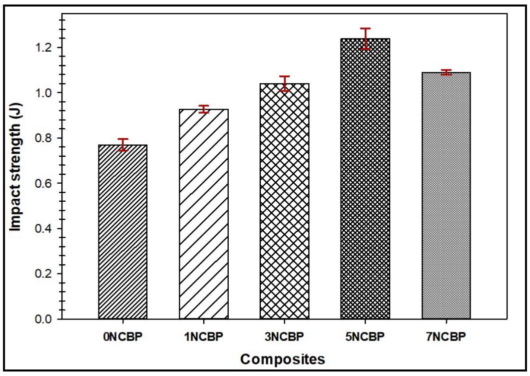

Figure 6: Impact strength of BP and NCBP hybrid composites

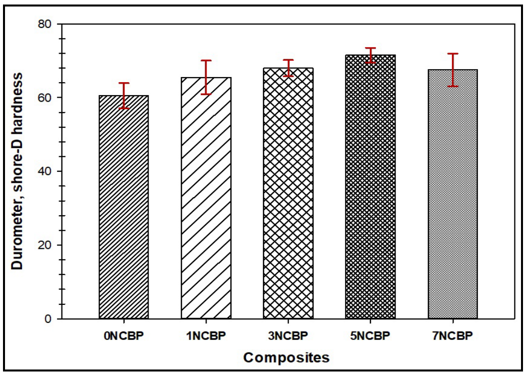

Figure 7: Shore-D hardness property of BP and NCBP hybrid composites

Table 3
Mechanical properties of NCBP composites and other bamboo fiber-based composites

Composites	Tensile strength (MPa)	Tensile Modulus (GPa)	Flexural strength (MPa)	Impact strength (KJ/m^2)	Ref.
Bamboo/PLA	29.39 to 39.51	1.71 to 2.17	55 to 64	6.46 to 8.89	25
Bamboo/PP/PLA	27 to 68	-	43 to 63	-	26
Bamboo/PP	31 to 36	0.9 to 1.1	44 to 53	-	27
Bamboo/Epoxy (layer based)	7.81 to 18.07	-	2.5 to 4.0	-	28
Bamboo/Polyester	36 to 56	61 to 90	-	11 to 12	29
Bamboo/Polyethylene	0.68 to 0.72	19 to 85	-	-	30
Bamboo/MUF	-	-	1.7 to 2.2	-	31
Bamboo/Silicon oil	18.50 to 23.80		20 to 29	11.8 to 12.8	32
Bamboo/Epoxy	262 to 363	6.1	11.2	-	33
Bamboo/Natural rubber	5 to 20	4.5	-	-	34
Bamboo/Rice husk/MWCNT	38.53 to 42.66	-	49.45 to 54.72	-	35
Bamboo/Epoxy/Cement by-pass dust	15 to 50	-	12 to 72	-	36
Bamboo/Polyester/TiO_2	50.4 to 63.56	-	79.54 to 92.70	-	37
Bamboo/Glass fiber/Polyester/Nanoclay	30 to 78.5	-	55.55 to 95.50	-	38
Bamboo fiber/Unsaturated polyester/Nanoclay (with different fiber orientation)	20.05 to 49.77	-	36 to 49.65	-	Present work

Vicat softening temperature (VST)

The VST of the neat and NCL filled BP hybrid composites is depicted in Figure 8. The VST of the neat BP composite was 51.25 °C. In the case of NCBP hybrid composites, the VST value increased from 55.88 to 65.22 °C as the NCL content was raised from 1 wt% to 5 wt% and beyond this, VST decreased to 61.25 °C at 7 wt%. This clearly indicates the impact of the NCL addition on the VST. It was found during the experimentation that the needle penetrated the neat BP composites at the temperature of 51.25 °C, which is comparatively lower than the temperatures for the NCBP hybrid composites. This may be ascribed to the fact that the inclusion of the NCL could have altered the rigidity of the composite system, resulting in increased hardness of the NCBP hybrid composites. Moreover, the surge in the temperature is not enough to break the bonds between the USP matrix, the bamboo fiber and the NCL, owing to the improvement in the stiffness of the material. Thus, it can be concluded that the stiffness property of the NCBP hybrid composites decides their VST.

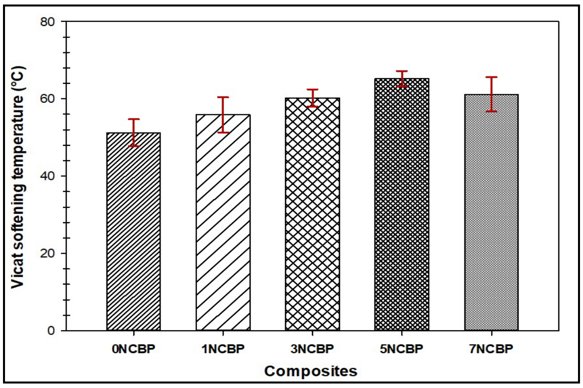

Figure 8: VST of BP and NCBP hybrid composites

Dynamic mechanical behavior of BP and NCBP hybrid composites

Storage modulus (E')

By understanding the storage modulus (E') behavior, the load bearing property of the composite materials can be predicted, as E' reflects the elastic components of the viscous elastic material. Moreover, the interfacial strength of fiber-matrix region, the toughness of the material system and the amount of cross-linking can also be comprehended. Figure 9 depicts the storage modulus (E') curves of the BP and NCBP hybrid composites. The solid portion of the E' curve reveals the bonding ability of the BP composites exposed to an increasing temperature, from which the stiffness and flexibility behavior of the material can be grasped. From the E' curves, it can be noted that the 5NCBP hybrid composite turned out to be the stiffest material amongst the neat and NCL filled BP hybrid composites. The highest E' modulus of 140.14 GPa was observed at the temperature of 31.39 °C. Even as the temperature increased, the E' modulus of the 5NCBP composite was noted to be superior to that of the other materials. For instance, the E' values at the temperatures of 60 °C and 80 °C were found to be 106.06 GPa and 62.22 GPa, respectively, which clearly indicates the positive impact of the NCL in the hybrid formulations. Irrespective of the material, an increasing temperature tends to decrease E', which shows the influence of the temperature on the mobility of the polymer chain, which further unfolds the flexibility of the composite material. Though the trend of E' modulus for all the NCL-filled hybrid composites was found to be similar, of them, the 7NCBP hybrid composite exhibited lower E' value. This may be ascribed to the excessive agglomeration of the NCL particles, which seems to prevent stress transfer to bamboo fibers via the matrix phase, thus exhibiting poor interfacial bonding between USP matrix-NCL-bamboo fiber.

Loss modulus (E")

The heat dissipation behavior and the viscous property of the BP and NCBP hybrid composites during increasing temperature can be studied by correlation with the loss modulus (E"). Figure 10 depicts the E" behavior of the BP and NCBP hybrid composites. It can be noted that all the NCBP specimens showed a similar trend, starting from the glassy to the rubbery region. When compared to the neat BP, the E" modulus of the NCL filled BP showed a promising trend, which may be due to the positive impact of hybridization on the properties of the composites. From the E" curves, it is evident that nearly 74.23% improvement in the loss modulus can be noted in the NCBP hybrid composites over the neat BP. This may be because hybridization causes internal friction, which may be sufficient to endorse the energy dissipation in the composite material. These arguments are in line with those in the literature.[1,24] Among the prepared samples, 5NCBP exhibited higher E" peak (207.91 MPa) than other laminates, probably owing to the higher energy dissipation caused by internal friction of the NCL filler. It is noteworthy that, as the temperature increased in the glass transition region, the E" modulus of all the composites showed a significant drop, which may be ascribed to the fact that the temperature played the role of a catalyst for the free mobility of the polymer chain.

Damping factor (Tanδ)

Damping factor is defined as the ratio of E' to E" denoted by Tanδ, which conveys the damping ability of the composite material. Moreover, the behavior of the material in the rubbery region can be understood from its damping property. The damping ratio of the NCBP composites is shown in Table 4. A higher damping ratio was noted for 0NCBP and a lower value – for the 5NCBP composites. A higher value indicates that the material is non-elastic due to the dissipation of energy and *vice versa*. Information on interphase bonding of the NCBP composites can be ascertained from their glass transition temperature (T_g), as indicated in Table 4.

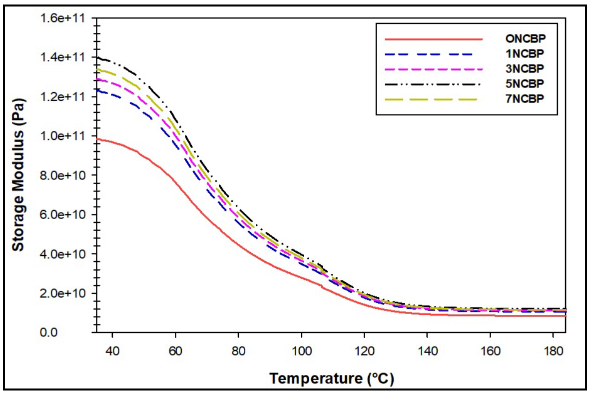

Figure 9: Storage modulus of BP and NCBP hybrid composites

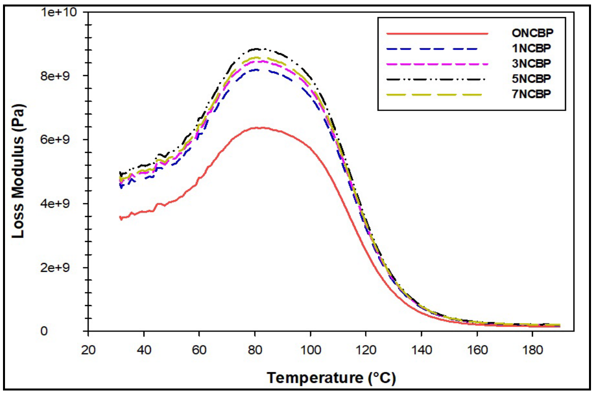

Figure 10: Loss modulus of BP and NCBP hybrid composites

Table 4
Viscoelastic properties and glass transition temperature (T_g) of NCBP hybrid laminates

Viscoelastic properties	Neat and NCL filled BP composites				
	0NCBP	1NCBP	3NCBP	5NCBP	7NCBP
E’ (GPa)	98.66	123.33	129.28	140.13	134.24
E” (MPa)	149.79	192.55	198.72	207.19	201.57
Damping factor (Tanδ)	0.2441	0.2175	0.2018	0.1890	0.1947
T_g (°C)	109.88	111.63	113.55	115.26	117.73

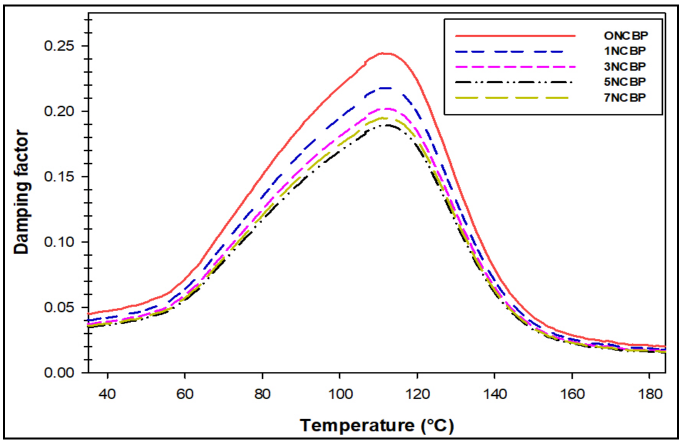

Figure 11: Damping property of BP and NCBP hybrid composites

From Figure 11, it can be noted that the damping peak values are lower in the 5NCBP and 7NCBP composites, which clearly conveys that these composites possess stronger interphase than the other NCBP composites. This could have happened owing to the restriction of the polymer chain due to the rigidity characteristics of the NCBP hybrid composites, eventually causing lesser dissipation. Moreover, it also indicates that these composites are of higher dynamic heterogeneity.

Thermogravimetric analysis

Figure 12 depicts the TGA curves of BP and NCBP hybrid composites. During the thermal degradation of the NCBP composites, an initial weight loss occurs between 80 °C and 160 °C, which is due to the removal of moisture from the composite surface. More significant weight loss of the composites was observed in the temperature range between 205 °C and 470 °C. This may be explained by the disintegration of the unsaturated polyester matrix. However, in general, chemical components of the bamboo fibers, such as hemicelluloses, cellulose, and lignin, are degraded in the temperature range of 160–480 °C.

Table 5 presents the TGA results of the NCBP composites. It is noted that, when the NCBP composites were exposed to temperatures beyond 480 °C, the formation of char residue was inevitable.[40] Also, the addition of the NCL increased the thermal stability of the NCBP hybrid composites. This may be attributed to the fact that NCL acts as a thermal shield, preventing volatilization and promoting char formation. Further, this developed char enhances the thermal resistance of the polymer. From the study, it is clearly evident that the char residue of the 5NCBP and 7NCBP composites is higher than that of the other NCBP composites, due to the inclusion of NCL. As compared to the BP composite, initial thermal degradation of the 1NCBP and 3NCBP composites increased to 218.77 °C and 227.59 °C, respectively. Also, their char residue was increased by 34.48% and 37.01%, with weight loss reduction of 77.28% and 75.96%, respectively. As for the 7NCBP composite, an initial degradation temperature of 284.49 °C, maximum thermal degradation of 460.17 °C and char residue of 25.95% are recorded. Besides, the 7NCBP composite exhibited lower weight loss, of 74.87%, and its char residue increased by 44.90%, 23.66%, and 12.44%, compared to 0NCBP, 1NCBP, and 3NCBP, respectively, which clearly indicated the effect of the NCL in the hybrid composites.

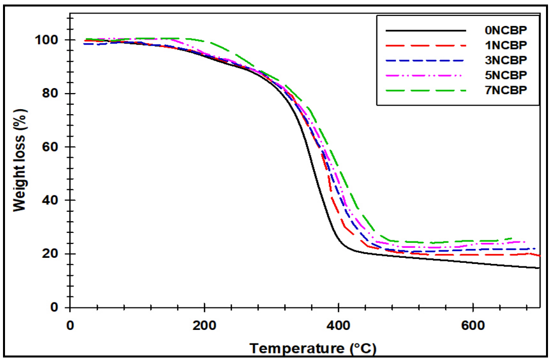

Figure 12: TG curves of BP and NCBP hybrid composites

Table 5
Thermal degradation and char development of NCBP composites

Composite laminates	Initial degradation temperature (°C)	Final degradation temperature (°C)	Weight loss (%)	Char residue (%)
0NCBP	207.68 ± 2.0	417.63 ± 3.0	77.93 ± 1.2	14.31 ± 0.7
1NCBP	218.77 ± 2.2	441.34 ± 2.8	77.28 ± 0.8	19.81 ± 0.6
3NCBP	227.59 ± 2.6	453.20 ± 2.5	75.96 ± 0.9	22.72 ± 0.5
5NCBP	266.66 ± 2.1	463.12 ± 2.6	75.32 ± 1.3	24.68 ± 0.5
7NCBP	284.49 ± 2.5	460.17 ± 3.1	74.87 ± 1.4	25.95 ± 0.3

From Table 5, it is noted that the final degradation temperature of the NCBP hybrid composites increased with the increase in the NCL, as it restricts the formation of the breakdown products. Apart from that, the NCL filler also helps in delaying the degradation temperature, thereby improves the thermal stability. It is further noted that the addition of NCL in the BP composites increases the thermal degradation temperature and increased the char residue content. From Table 5, it is observed that 5NCBP exhibited higher thermal stability than other laminates, and this may be because the dispersed NCL filler enhances the interfacial adhesion between the fiber and the matrix, which paves the way for the formation of a homogenous structure in the composites, resulting in an increased ability of the material to resist heat and thermal degradation. However, higher than 5 wt% addition of NCL results in lower thermal stability of the composites, owing to poor dispersion of the NCL caused by the agglomeration process. Further, it is interesting to see that 7NCBP has higher char residue than other NCBP composites, because the increased amount of inorganic NCL remains after thermal decomposition.

FESEM analysis of fractured BP and NCBP hybrid composites

From Figure 13, it is interesting to note that the 5NCBP composite is found denser in structure, and the space among the bamboo fibers is very low, compared with the 3NCBP composite. Hence, tensile strength increased due to the effective transfer of load from the polyester matrix to the surrounding bamboo fibers. Moreover, agglomeration of the NCL at the proximity of the fiber-matrix region is evident, which may result in reduction of the tensile strength in the NCBP hybrid composites. When the composite materials are subjected to tensile loading, NCL particles adhering to the surface of the laminates may be prone to detaching, thereby creating voids, which may cause premature failure of the composites, as indicated in Figure 14. Fiber pullout in the 3NCBP composite after the flexural/bending failure is evident. This conveys poor interfacial bonding between the NCL filler, the bamboo fiber and the USP matrix. On the other hand, the 5NCBP composites showed significant fiber breakage, along with debris of the matrix, which implies the bonding between the reinforcing agent and the matrix phase is stronger due to the addition of NCL. Hence, fiber breakages take place only when the applied load exceeds the ultimate tensile strength of the fiber, especially when the composite surface experiences tension (tensile force) during the bending load. Thus, when the NCL filler is added, bending strength increases.

Generally, the presence of the NCL filler has a major effect on various aspects, such as fiber breakages, matrix fracture, filler detachment, voids, delamination, fiber stretching, pull outs, and porosity, as revealed by FESEM. 5NCBP showed stronger interfacial bonding and lesser fiber fracture, as compared to the 7NCBP composites.

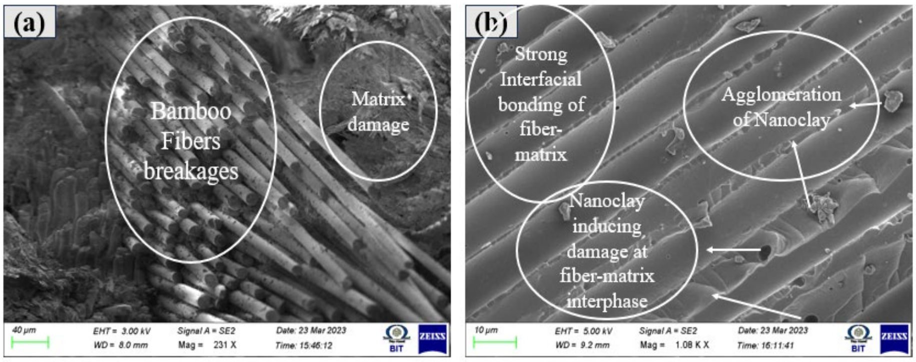

Figure 13: FESEM images of the tensile fractured surfaces of (a) 5NCBP, and (b) 3NCBP hybrid composites

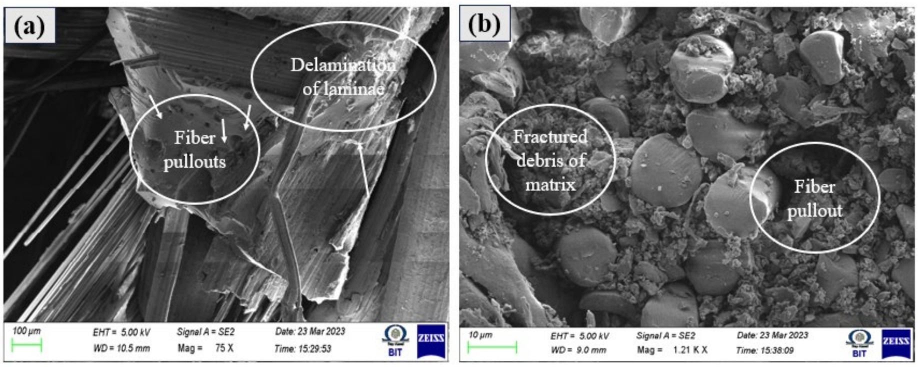

Figure 14: FESEM images of the flexural fractured surfaces of (a) 3NCBP, and (b) 5NCBP hybrid composites

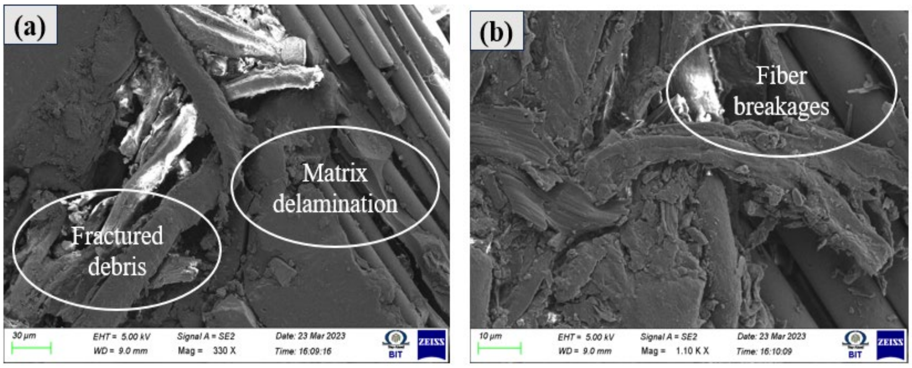

Figure 15: FESEM images of the flexural fractured surfaces of (a) 5NCBP, and (b) 7NCBP hybrid composites

Moreover, fiber pullouts, fractured matrix and debris agglomeration (Fig. 15) are more pronounced in the latter composites, which may be caused by poor bonding between the reinforcing agent and the USP matrix, and excess agglomeration of the NCL particles. Therefore, the 5NCBP hybrid composites exhibited comparatively better mechanical properties than the other NCBP composites.

CONCLUSION

From the present study, the following conclusions can be drawn.

- The addition of the NCL filler in BP composites significantly influenced the mechanical properties of the hybrid composites. Higher tensile strength was revealed by the 5NCBP hybrid composite (49.77 MPa). The same composition (5 wt% of NCL filler in BP composite) showed a positive impact on other mechanical properties as well, such as flexural, impact and shore-D hardness.
- In the case of flexural strength, no significant improvement was noticed between the 3NCBP and the 7NCBP hybrid composites. However, if their impact strength is concerned, some notable development was observed in the range from 20.38% to 60.88%, comparing the neat BP to the 7NCBP hybrid composites.
- The VST of the NCBP hybrid composites increased from 51.25 °C to 65.22 °C. Their thermal stability enhanced to some extent as the NCL acts as a thermal shield, preventing volatilization and helps char formation.
- The dynamic mechanical analysis suggests that the E' and E" moduli of the NCBP hybrid composites were superior to those of the neat BP composites. Overall, the 5NCBP composite showed a significant improvement in loss modulus – of 74.23% – compared to the neat BP composites. The higher damping value and the shifting of the glass transition temperature indicated the positive impact of the addition of NCL in BP composites. This may be attributed to the uniform distribution of the NCL filler and strong interaction among the bamboo fiber, the USP matrix and NCL.
- The addition of higher NCL loadings (beyond 5 wt%) deteriorates the mechanical, thermal and viscoelastic properties of the NCBP hybrid composites. FESEM images of the fractured NCBP hybrid composite revealed agglomeration of nanoclay particles, fiber pull-outs, matrix damage, delamination of layers, and fiber breakages.

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